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(54) Grout powder having been admixed with a fluorochemical compound

(57) The invention relates to grout powder for admixture with water to produce grout. The grout powder comprises cement powder and is characterized in that the grout powder has been mixed with a fluorochemical compound. The present invention further relates to a method of preparing grout powder for admixture with water to produce grout, comprising mixing grout powder

comprising cement powder with a fluorochemical compound. Still further, the invention relates to an alternative method for making the grout powder, which method comprises treating at least one of the components of the grout powder with a fluorochemical compound.

EP 1 262 464 A1

Description**1. Field of the invention**

5 [0001] The present invention relates to grout powder for producing grout upon admixture with water. In particular, the present invention relates to grout powder that has been mixed with a fluorochemical compound.

2. Background of the invention

10 [0002] As is well known, spaces between tiles that are fixed to a wall or floor are typically filled with grout, which is produced by mixing grout powder with water. Because of the presence of cement powder, the grout upon drying will cure and effectively adhere and fill the spaces between the tiles. For improving the stain repellency, the tiles may have been surface treated with a fluorochemical composition which generally also provides water and oil repellency to the tile surface. Such is for example of particular interest for bathroom tiles. For example, it has been disclosed to use a fluorochemical silane to treat for example the surfaces of tiles to render these oil- and water repellent as illustrated for example by US 5,608,003, US 5,442,011, US 5,550,184 and US 5,274,159.

15 [0003] However, while the tile surface is thereby rendered repellent to water, oil and dirt, the grout spaces between them, when left untreated, would still pick up dirt thereby somewhat reducing the benefits of having treated tiles. Accordingly, it has already been proposed to also treat the surface of the grout between the tiles with a fluorochemical compound in order to effect repellency properties also to the grout. For example, GB 2,218,097 and US 5,209,775, disclose treatment of tiles as well as cured cement materials or the surface of a grout with a fluorochemical silane compound.

20 [0004] Although these treatments of the grout surface are effective, the durability of the treatment leaves a desire for further improvement. Also, applying the treatment to a grout, filling a space between tiles, would be highly labor intensive and therefore costly.

25 [0005] It would thus be desirable to provide oil- and/or water repellency as well as stain repellency to grout in a cost effective way and preferably with improved durability.

3. Summary of the invention

30 [0006] It has now been found that by mixing a fluorochemical compound with the grout powder from which grout is normally produced by mixing the powder with water, a grout can be obtained that has desirably oil-, water- and/or stain-repellency properties in a cost effective and convenient way. In particular, no separate additional treatment of the grout is needed after its application between for example tiles to fill spaces there between. Additionally, the durability of the treatment is improved relative to a treatment of the same fluorochemical compound to the surface of the grout. Surprisingly, although the fluorochemical compound is admixed in the mass of the grout powder and would thus be expected to be available in lesser amounts at the surface compared to a topical treatment of the grout with the fluorochemical compound, only small amounts of the fluorochemical compound are needed and the adherence of the grout between tiles is thereby not adversely affected.

35 [0007] Thus, in one aspect, the invention relates to grout powder for admixture with water to produce grout, said grout powder comprising cement powder, characterized in that said grout powder has been mixed with a fluorochemical compound.

[0008] The present invention further relates to a method of preparing grout powder for admixture with water to produce grout, comprising mixing grout powder comprising cement powder with a fluorochemical compound.

40 [0009] Still further, the invention relates to an alternative method for making the grout powder, which method comprises treating at least one of the components of said grout powder with a fluorochemical compound.

4. Detailed description

50 [0010] The fluorochemical compound for use with the invention is typically a compound that has one or more fluorinated groups which can be monovalent or multivalent such as for example divalent. The fluorochemical compound can be polymeric, oligomeric or a simple fluorinated organic compound. Examples of fluorinated groups include in particular fluoroaliphatic groups, which are stable, inert, preferably saturated and non-polar as well as fluorinated polycyclic groups. The fluoroaliphatic group may be straight chain, branched-chain, or cyclic or combinations thereof and may contain one or more heteroatoms such as oxygen, divalent or hexavalent sulfur, or nitrogen. The fluorinated group(s) are preferably fully-fluorinated, but hydrogen or chlorine atoms can be present as substituents if not more than one atom of either is present for every two carbon atoms. Suitable fluorinated groups generally have at least 3 and up to 18 carbon atoms, preferably 3 to 14, especially 4 to 10 carbon atoms, and preferably contain about 40% to about 80%

fluorine by weight, more preferably about 50% to about 79 % fluorine by weight. The terminal portion of the fluorinated group is typically a perfluorinated moiety, which will preferably contain at least 7 fluorine atoms, e.g., $\text{CF}_3\text{CF}_2\text{CF}_2^-$, $(\text{CF}_3)_2\text{CF}^-$, F_5SCF_2^- . The preferred fluorinated groups are fully or substantially fluorinated and include those perfluorinated aliphatic radicals of the formula $\text{C}_n\text{F}_{2n+1}^-$ where n is 3 to 18, particularly 4 to 10.

- 5 [0011] Examples of useful fluorochemical compounds include, for example fluorinated group containing urethanes, ureas, esters, amines (and salts thereof), amides, acids (and salts thereof), carbodiimide, guanidines, allophanates, biurets, oxazolidinones, and other substances containing one or more fluorinated groups, as well as mixtures and blends thereof. Such agents are well known to those skilled in the art, see e.g. Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Ed., Vol. 24, pp 448-451 and many are commercially available as ready-made formulations. Useful
10 fluorochemical compounds can be polymers containing multiple fluorinated groups such as polymers of fluorochemical acrylate and/or methacrylate monomers with copolymerizable non-fluorinated monomers. Such compounds include, for example, those described in US 3,330,812, US 3,341,497, US 3,318,852, US 4,013,627 and WO 9916809. Further examples of fluorochemical compounds useful in the invention include those formed by the reaction of fluorinated, e.g. perfluoroaliphatic, organic compounds containing an active hydrogen with diisocyanates to provide fluorinated group-bearing polyurethanes. Such reaction products are described, for example, in US 3,398,182. Another group of fluorochemical compounds are fluorinated radical-containing N-methylolcondensation products. These compounds are described in US 4,477,498. Further examples include fluorinated radical-containing polycarbodiimides which can be obtained by, for example, reaction of perfluoroaliphatic sulfonamido alkanols with polyisocyanates in the presence of suitable catalysts. Further examples of fluorochemical compounds include fluorinated carboxylates, as described in, 15 for example, US 4,681,790 or fluorinated phosphates, such as described in US 3,094,547.

20 [0012] The fluorochemical compounds for admixture with the grout powder include compounds that have one or more groups capable of reacting with one or more components of the grout powder as well as compounds that do not contain such reactive groups. Preferably, the fluorochemical compound includes at least one group capable of reacting with one or more components of the grout powder. A particularly suitable group capable of such reaction is a silyl group 25 that has one or more hydrolyzable groups.

25 [0013] Examples of fluorochemical compounds capable of reacting with the grout powder or one of its components include those that can be represented by the formula I:

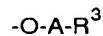


30 wherein R_f represents a fluorinated organic group for example as described above, n being 1 or 2 and Y represents an alkyl group, an aryl group or a hydrolysable group. Each Y can be the same or different and at least one Y group is a hydrolysable group. Y can be for example a C_1-C_{30} alkyl group, which may be straight chained or branched and 35 may include one or more aliphatic, cyclic hydrocarbon structures, a C_6-C_{20} aryl group (optionally substituted by one or more substituents selected from halogens and C_1-C_4 alkyl groups), or a C_7-C_{20} aralkyl group.

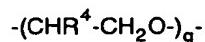
40 [0014] Suitable hydrolysable groups include those that are generally capable of hydrolyzing under appropriate conditions of admixture with the grout powder or one of its components, for example under aqueous, acidic or basic conditions, such that the fluorochemical silane compound can undergo condensation reactions. Preferably, the hydrolysable groups upon hydrolysis yield groups capable of undergoing condensation reactions, such as silanol groups.

45 [0015] Examples of hydrolysable groups include halide groups, such as chlorine, bromine, iodine or fluorine, alkoxy groups -OR' (wherein R' represents a lower alkyl group, preferably containing 1 to 6, more preferably 1 to 4 carbon atoms and which may optionally be substituted by one or more halogen atoms), acyl groups, acyloxy groups -O(CO)-R" (wherein R" represents a lower alkyl group, preferably containing 1 to 6, more preferably 1 to 4 carbon atoms, which may be optionally substituted by one or more halogen atoms), aryloxy groups -OR''' (wherein R''' represents an aryl moiety, preferably containing 6 to 12, more preferably containing 6 to 10 carbon atoms, which may be optionally substituted by one or more substituents independently selected from halogens, and C_1-C_4 alkyl groups which may 50 optionally be substituted by one or more halogen atoms). In the above formulae R', R", and R''' may include branched structures.

50 [0016] Suitable hydrolysable groups also include polyoxyalkylene groups of the formula



55 wherein A is a divalent hydrophilic group having the formula



5 wherein q is a number having a value of 1 to 40, preferably 2 to 10, R⁴ is hydrogen or methyl, and at least 70% of R⁴ is hydrogen, and R³ independently is hydrogen or a lower alkyl group having 1 to 4 carbon atoms, such as disclosed in US-A-5,274,159. Specific examples of hydrolysable groups include methoxy, ethoxy and propoxy groups, chlorine and an acetoxy group. Particularly preferred hydrolysable groups include C₁-C₄ alkoxy groups, such as methoxy and ethoxy groups.

10 [0017] In a particularly preferred embodiment, R_f in formula I corresponds to the formula II :



15 wherein X represents an organic linking group or a chemical bond. The divalent linking group X can include linear, branched, or cyclic structures, that may be saturated or unsaturated. The group X is generally non-fluorinated and can contain one or more heteroatoms (e.g., oxygen, nitrogen, or sulfur) or functional groups (e.g., carbonyl, amido, urethane, or sulfonamido). Preferably, the divalent linking group X is a hydrocarbon group, preferably, a linear hydrocarbon group, optionally containing heteroatoms or functional groups, and more preferably, containing at least one functional group. Examples of X groups include -C(O)NH(CH₂)₃-, -CH₂O(CH₂)₃-, -CH₂OC(O)N(R)(CH₂)₃-, wherein R is H or lower alkyl group, and -(C_nH_{2n})-, wherein n is about 2 to about 6. A preferred linking group X is -C(O)NH(CH₂)₃- and -OC(O)NH(CH₂)₃-.

20 [0018] In one embodiment, R_f^a represents a perfluorinated aliphatic radical having at least 3 carbon atoms. In an further embodiment, R_f^a represents a partially or fully fluorinated (i.e., all C-H bonds are replaced by C-F bonds) polyether group including perfluorinated repeating units selected from the group of -(C_nF_{2n})-, -(C_nF_{2n}O)-, -(CF(Z))-, -(CF(Z)O)-, -(CF(Z)C_nF_{2n}O)-, -(C_nF_{2n}CF(Z)O)-, -(CF₂CF(Z)O)-, and combinations thereof. In these repeating units Z is a perfluoroalkyl group, an oxygen-substituted perfluoroalkyl group, a perfluoroalkoxy group, or an oxygen-substituted perfluoroalkoxy group, all of which can be linear, branched, or cyclic, and preferably have about 1 to about 9 carbon atoms and 0 to about 4 oxygen atoms. The terminal groups can be (C_nF_{2n+1})-, (C_nF_{2n+1}O)- or (X'C_nF_{2n}O)-, wherein X' is H, Cl, or Br, for example. Preferably, these terminal groups are perfluorinated. In these repeating units or terminal groups, n is 1 or more, and preferably 1 to 4. Particularly preferred approximate average structures for a perfluoropolymers include C₃F₇O(CF(CF₃)CF₂O)_pCF(CF₃) and CF₃O(C₂F₄O)_pCF₂ where an average value for p is 1 to about 50. Examples of polyfluoropolyethers made of these repeating units are disclosed in U.S. Pat. No. 5,306,758 (Pellerite).

30 [0019] In still another embodiment, R_f^a represents a fluorinated oligomer of formula M^f_sM^h_t wherein M^f represents units derived from a fluorinated monomer, M^h represents units derived from non-fluorinated monomers, s represents a value of 1 to 40, t represents a value of 0 to 40 and the sum of s and t is at least 2.

35 [0020] The units M^f are generally derived from fluorochemical monomers corresponding to the formula :



40 wherein R_f^b represents a fluoroaliphatic group containing at least 3 carbon atoms or a fluorinated polyether group. Q represents an organic divalent linking group and E¹ represents a free radical polymerizable group.

45 [0021] Fluorochemical monomers R_f^b-Q-E¹ as described above and methods for the preparation thereof are known and disclosed, e.g., in U.S. Pat. No. 2,803,615. Examples of such compounds include general classes of fluorochemical acrylates, methacrylates, vinyl ethers, and allyl compounds containing fluorinated sulfonamido groups, acrylates or methacrylates derived from fluorochemical telomer alcohols, acrylates or methacrylates derived from fluorochemical carboxylic acids, and perfluoroalkyl acrylates or methacrylates as disclosed in EP-A-526 976. Fluorinated polyether-acrylates or methacrylates are described in U.S. Pat. No. 4,085,137.

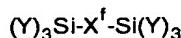
50 [0022] The units M^h are generally derived from a non-fluorinated monomer, preferably a monomer consisting of a polymerizable group and a hydrocarbon moiety. Hydrocarbon group containing monomers are well known and generally commercially available. Useful hydrocarbon containing monomers include those according to formula:



55 wherein R^h represents a hydrocarbon group, Q¹ is a divalent linking group, s is 0 or 1 and E² is a free radical polym-

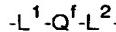
erizable group. Examples of linking groups Q¹ include oxy, carbonyl, carbonyloxy, carbonamido, sulphonamido, oxy-alkylene and poly(oxyalkylene). Examples of non-fluorinated monomers from which the units M^h can be derived include general classes of ethylenic compounds capable of free-radical polymerization.

[0023] Fluorochemical compounds having a divalent fluorinated organic group include for example those that correspond to the formula:



10 wherein Y represents an alkyl group, or a hydrolysable group as defined above and X^f representing a fluorinated or perfluorinated organic divalent group.

In a particularly preferred embodiment X^f corresponds to the formula:



15 wherein L¹ and L² each independently represents an organic divalent linking group or a chemical bond and Q^f represents a perfluorinated aliphatic group of at least 3 carbon atoms. Examples of Q^f include divalent polyfluoropolyether that can include linear, branched, and/or cyclic structures, that may be saturated or unsaturated, and substituted with one or more oxygen atoms. Q^f preferably is a perfluorinated group (i.e., all C-H bonds are replaced by C-F bonds). More preferably, it includes perfluorinated repeating units selected from the group of -(C_nF_{2n}O)-, -(C_nF_{2n}O)-, -(CF(Z))-, -(CF(Z)O)-, -(CF(Z)C_nF_{2n}O)-, -(C_nF_{2n}CF(Z)O)-, -(CF₂CF(Z)O)-, and combinations thereof, wherein the repeating units generally may be randomly, blocky or alternating arranged.

[0024] In these repeating units Z is a perfluoroalkyl group, an oxygen-substituted perfluoroalkyl group, a perfluoroalkoxy group, or an oxygen-substituted perfluoroalkoxy group, all of which can be linear, branched, or cyclic, and preferably have about 1 to about 9 carbon atoms and 0 to about 4 oxygen atoms. Examples of polyfluoropolymers containing polymeric moieties made of these repeating units are disclosed in U.S. Pat. No. 5,306,758 (Pellerite).

[0025] Preferred approximate average structures for a divalent perfluoropolyether group include -CF₂O(CF₂O)_m(C₂F₄O)_pCF₂-, wherein an average value for m is 0 to about 50 and an average value for p is 0 to about 50, with the proviso that both m and p are not simultaneously 0, -CF(CF₃)O(CF(CF₃)CF₂O)_pCF(CF₃)-, -CF₂O(C₂F₄O)_pCF₂-, and -(CF₂)₃O(C₄F₈O)_p(CF₂)₃-, wherein an average value for p is 3 to about 50. The repeating units characterized by m and p generally may be randomly, blocky or alternating arranged. Of these, particularly preferred approximate average structures are -CF₂O(CF₂O)_m(C₂F₄O)_pCF₂-, -CF₂O(C₂F₄O)_pCF₂-, and -CF(CF₃)O(CF(CF₃)CF₂O)_pCF(CF₃)-.

[0026] As synthesized, these structures typically include a mixture of polymeric units. The approximate average structure is the approximate average of the mixture of structures. The divalent linking groups L¹ and L² may be the same or different and can include linear, branched, or cyclic structures, that may be saturated or unsaturated, and preferably contain 1 to 15 atoms. The groups L¹ and L² can contain one or more heteroatoms (e.g., oxygen, nitrogen, or sulfur) and/or one or more functional groups (e.g., carbonyl, amido, urethylene or sulfonamido). It can also be substituted with one or more halogen atoms (preferably, fluorine atoms), although this is less desirable, as this might lead to instability of the compound. The divalent linking groups L¹ and L² preferably are substantially stable against hydrolysis.

[0027] For example, L¹ and L² may be a saturated or unsaturated hydrocarbon group typically including 1 to 15 carbons atoms. Preferably L¹ and L² are linear hydrocarbon groups preferably containing 1 to 10 carbon atoms, and optionally containing 1 to 4 heteroatoms and/or 1 to 4 functional groups, and more preferably, containing at least one functional group.

[0028] Examples of L¹ and L² groups include -C(O)NH(CH₂)₃-, -CH₂O(CH₂)₃-, -OC(O)NH(CH₂)₃- and -CH₂OC(O)N(R)(CH₂)₃-, wherein R is H or lower alkyl group (preferably containing 1 to 4 carbon atoms, such as methyl, ethyl, n- and iso-propyl, and n-and iso-butyl), and -(C_nH_{2n}O)-, wherein n is about 2 to about 6. Preferred linking groups L¹ and L² are -C(O)NH(CH₂)₃- and -OC(O)NH(CH₂)₃-.

[0029] Fluorochemical compounds suitable for use in the grout powder typically have a molecular weight (number average) of at least about 400, and preferably, at least about 500. Preferably, they are no greater than about 100000.

[0030] The fluorochemical compound may be used as a solution or dispersion in one or more organic solvents. Suitable organic solvents, or mixtures of solvents can be selected from aliphatic alcohols (preferably containing 1 to 6 carbon atoms), such as methanol, ethanol, isopropylalcohol ; ketones such as acetone or methyl ethyl ketone ; esters, such as ethyl acetate, methylformiate, ethers, such as diethyl ether and alkanes, such as heptane. Mixtures of solvents may be used. Particularly preferred solvents include ethanol and acetone.

[0031] Fluorinated solvents may be used in combination with the organic solvents in order to improve solubility of the fluorochemical compound. Examples of fluorinated solvents include fluorinated hydrocarbons, such as perfluoro-

hexane or perfluorooctane, available from 3M; partially fluorinated hydrocarbons, such as pentafluorobutane, available from Solvay, or $\text{CF}_3\text{CFHCFHCF}_2\text{CF}_3$, available from DuPont; hydrofluoroethers, such as methyl perfluorobutyl ether or ethyl perfluorobutyl ether, available from 3M. Various blends of these materials with organic solvents can be used.

[0032] The fluorochemical composition may include further additives. For example, in case the fluorochemical compound is a fluorochemical silane, the composition will generally include water, in order to facilitate the reaction of the fluorochemical silane with the surface of one or more of the components of the grout powder although humidity in the powder or air may suffice as well. Preferably, the amount of water will be between 0.1 and 20% by weight. More preferably between 1 and 10% by weight. In addition to water, a fluorochemical silane containing composition may also include an organic or inorganic acid or a base. Organic acids include acetic acid, citric acid, formic acid and the like ; fluorinated organic acids, such as $\text{CF}_3\text{SO}_3\text{H}$, $\text{C}_3\text{F}_7\text{COOH}$, $\text{C}_7\text{F}_{15}\text{COOH}$, $\text{CF}_3(\text{CF}_2)_2\text{OCF}(\text{CF}_3)\text{COOH}$ or $\text{C}_3\text{F}_7\text{O}(\text{CF}(\text{CF}_3)\text{CF}_2\text{O})_{10-30}\text{CF}(\text{CF}_3)\text{COOH}$, commercially available from DuPont. Examples of inorganic acids include sulphuric acid, hydrochloric acid and the like. Examples of useful bases include sodium hydroxide, potassium hydroxide and triethylamine. The acid or base will generally be included in the composition in an amount between about 0.01 and 10%, more preferably between 0.05 and 5% by weight.

[0033] Grout powder for admixture with water to produce grout typically comprises cement, such as Portland cement, in amounts between about 30 % and 50 % by weight and quartz in amounts between 50 % and 70 % by weight. Other additives, such as glass bubbles, epoxyresins, silicone resins and acrylic resins may be added. The additives will typically be used in amounts between about 0 and 10%, preferably between 0 and 5% by weight. The grout powder for admixture with water to produce grout, can be treated or mixed with a fluorochemical compound by mixing the fluorochemical compound with the grout powder or mixing it with one or more components thereof and then mixing these components with the other components of the grout powder. Generally, the obtained grout powder will have the fluorochemical compound distributed throughout the mass of the grout powder.

[0034] Thus, in accordance with one embodiment to produce the grout powder, the fluorochemical compound, dissolved or dispersed in solvent, optionally containing water and acid or base, may be mixed with dry grout powder. The mixture of grout powder and fluorochemical compound can typically be dried at a temperature between about 30°C and 150°C, preferably at a temperature between 60°C and 120°C and for a time sufficient to dry the grout powder.

[0035] In an alternative way, the fluorochemical compound, preferably dissolved or dispersed in solvent, optionally containing water and acid or base, can be mixed with a component that will be a constituent of the final grout powder. That component is then mixed with the other components of the grout powder to obtain the grout powder having admixed therewith the fluorochemical compound. The mixture of the grout component and fluorochemical compound can be dried at a temperature between about 30°C and 150°C, preferably at a temperature between 60°C and 120°C and for a time sufficient to dry the component. Suitable grout components that may be so admixed or treated with the fluorochemical compound include for example quartz, cement or certain additives of the grout powder such as glass bubbles.

[0036] To obtain the final grout for filling for example spaces between ceramic tiles, the grout powder is generally admixed with water.

[0037] The amount of the fluorochemical compound that will generally be contained in the grout powder in accordance with the invention is chosen so that sufficiently high oil and water repellency properties and/or stain repellency properties are imparted to the final grout produced therefrom. This amount is usually such that 0.01 % to about 5 % by weight, preferably 0.05 % to about 3 % by weight, based on the weight of the grout powder, of fluorochemical compound is present in the grout powder. The amount of fluorochemical compound is preferably kept below 5%, in order to avoid that the grout becomes too repellent by itself and/or that adhesion problems between the grout and the substrate occur. The amount which is sufficient to impart desired properties can be determined empirically and can be increased as necessary or desired. The amount of fluorchemical compound used in the grout powder will generally be such that amount sufficient to produce grout which is water and oil repellent, such a grout having at 20°C a contact angle with distilled water of at least 70°, and a contact angle with n-hexadecane of at least 30°, measured after drying and curing of the grout.

[0038] The fluorochemical compound may be used together with further additives that provide the grout with additional beneficial properties, such as antimicrobial or fungicidal properties. Examples include $\text{C}_{18}\text{H}_{37}\text{N}^+(\text{CH}_3)(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3\text{Cl}^-$. However, the addition of ionic additives is preferably kept below about 10% by weight, in order not to adversely affect the water repellency properties of the composition. The use of the fluorochemical compound in the grout powder results in rendering the grout less retentive of soil and more readily cleanable due to the oil and water repellent nature of the treated grout. These desirable properties are maintained despite extended exposure or use and repeated cleanings because of the high degree of durability of the treated grout as can be obtained through the compositions of this invention.

[0039] The mixture of grout powder, comprising fluorochemical compound, and water can be applied by simple means of a spatula or a pointing-trowel in between pre-glued tiles. About 30 minutes after application of the grout mixture, the excess grout can typically be removed by means of a wet sponge. The tiles and semi-dried grout can subsequently

be wiped with a wet cloth, so as to reestablish the original esthetics of the tile and to smoothen the grout filling. After drying for 24 hours at room temperature, the grout filling can be considered to be complete.

[0040] The grout powder is preferably used to fill spaces between tiles, in particular ceramic tiles, that have been or that are being treated with fluorochemical compound, in particular with fluorochemical compounds that have a one or more silyl groups such as the silyl group containing compounds described above. As result, a complete surface durable oil- and water repellent can be achieved in a convenient and cost effective way.

EXAMPLES

[0041] The following examples further illustrate the invention without the intention however to limit the invention thereto. All parts are by weight unless indicated otherwise.

Abbreviations

[0042] HFE-7100 : methyl perfluorobutylether, available from 3M

FC-1 : 60 % solution of N-methyl-N-[3-trichlorosilyl]propyl]-perfluorooctylsulfonamide in ethanol, prepared essentially according to GB 2218097, example 1.

FC-2 : 30 % solution of fluorochemical acrylate copolymer in ethyl acetate/heptane, prepared by reacting N-methyl perfluorooctyl sulfonamido ethyl methacrylate with octadecylmethacrylate in a ratio 65/35. The polymerization reaction was done under nitrogen atmosphere, in a solvent mixture of ethyl acetate/heptane 70/30 at 30% solids, using AIBN as initiator.

FC-3 : 30 % solution of fluorochemical urethane (PAPI/N-ethyl perfluorooctyl sulfonamido ethyl alcohol/2-ethyl-hexanol 9.8/27.1/3.1) in ethyl acetate, prepared as follows : the reagents were placed in a three necked flask, equipped with a stirrer, heating mantle, thermometer and condenser, in a ratio as given above. Ethyl acetate was added to obtain a 30 % solids mixture. The reaction mixture was heated to 50°C under nitrogen atmosphere. DBTDL catalyst was added and the mixture was heated to reflux until all isocyanate had reacted.

FC-4 : 2% solution of a copolymer of perfluoroheptyl methylmethacrylate/acrylic acid 98/2, in HFE 7100, made essentially according to WO 9916809, example 12.

FC-5 : fluorochemical polyetherdisilane, prepared by reacting perfluoropolyetherdiester $\text{CH}_3\text{OC(O)CF}_2(\text{CF}_2\text{O})_{9-11}(\text{CF}_2\text{CF}_2\text{O})_{9-11}\text{CF}_2\text{C(O)OCH}_3$ (with average molecular weight of about 2000), commercially available from Ausimont, Italy, under the trade designation Z-DEAL, with 3-aminopropyltrimethoxysilane, available from Aldrich Company Co., as taught in US 3,810,874 (Mitsch et al.), table 1, line 6. The exothermic reaction proceeded readily at room temperature, simply by mixing the starting materials. The progress of the reaction was monitored by infrared analysis.

PAPI: polyaromatic polymethylene polyisocyanate, available from Dow Chemical

Grout application

[0043] A mixture of grout powder, comprising fluorochemical compound, and water was applied in between pre-glued tiles, available from Jasba, by means of a spatula. After 30 minutes, the excess grout was removed with a wet cloth. The grout was allowed to dry at room temperature during 24 hours. The dried grout was abraded 20 times using a wet Scotch-Brite™ sponge.

Contact angles

[0044] Dried grout was tested for water- and oil repellency, by measuring the contact angles versus respectively water (W) and n-hexadecane (O), using an Olympus TGHM goniometer. The contact angles were measured before ("initial") and directly after the samples were abraded 20 times with a wet Scotch-Brite™ sponge ("abrasion"). The values were the mean values of 4 measurements and were reported in degrees. The minimum measurable value for a contact angle was 20. A value <20 meant that the liquid spread on the surface. A contact angle with distilled water of at least 70° was indicative of good water repellency ; a contact angle with n-hexadecane of at least 30° was indicative of good oil repellency.

EXAMPLESExamples 1 to 3 and comparative examples C-1 to C-3

[0045] In example 1, 100 g dry grout powder, comprising 40% Portland cement and 60% quartz, was mixed with 100 g fluorochemical composition comprising 2 g FC-1, 3 g acetic acid, 10 g water and 85 g ethanol. In examples 2 and 3, 100 g dry grout powder, comprising 40% Portland cement and 60% quartz, was mixed with 3 g of FC-3 (Ex 2) or 3g of FC-2 (Ex 3), dissolved in 20 g ethyl acetate. After mixing, the grout powders were dried at 120°C during 15 minutes. Water was added and the grout was stirred to make a homogeneous, coagulate-free mixture. Comparative example C-1 was made with grout that did not contain the fluorochemical compound (mixture of grout powder, comprising 40% Portland cement and 60% quartz, and water). Each of the grout mixtures was applied in between pre-glued tiles according to the general method. The grout was allowed to dry at room temperature during 24 hours.

In comparative examples C-2 and C-3 the grout was made in the same way as comparative example C-1, i.e. no fluorochemical compound was mixed in the grout, but the obtained dried and cured grout was subjected to a topical treatment with a fluorochemical compound. Therefore, the dried untreated grout as prepared according to comparative example 1 was treated with a mixture comprising 3% FC-1, 3% acetic acid, 10% water and 84% ethanol through a brush application at about 100 ml/m² (comparative example 2). In comparative example C-3 FC-4 was used instead of FC-1. The topically treated grout was allowed to dry at room temperature during 24 hours.

The grout of the examples and comparative examples was abraded 20 times with a wet Scotch-Brite™ sponge. Contact angles were measured before and after abrasion. The results are given in table 1.

Table 1 :

Contact angles of grout obtained from grout powder mixed with fluorochemical compound					
Ex	Fluorochemical compound	Contact angles (°)			
		Initial Water	Initial hexadecane	Abrasion Water	Abrasion hexadecane
1	FC-1	95	60	85	55
2	FC-3	90	68	80	60
3	FC-2	80	65	70	50
C-1	/	<20	<20	<20	<20
C-2	FC-1 (topical treatment)	95	65	50	25
C-3	FC-4 (topical treatment)	110	68	55	22

[0046] As can be seen from table 1, the results indicate that grout with high oil and water repellency could be made, when the grout powder had been treated with a fluorochemical compound. Not only high initial oil and water repellency was obtained, but also after abrasion, indicating high durability of the treatment. Untreated grout did not show any oil- and/or water repellency. A topical treatment with fluorochemical compounds provides grout with initial good oil- and water repellency. However the performance drops after abrasion, indicating low durability of the treatment.

Examples 4 and 5

[0047] In example 4, 100 g dry quartz was treated with 100 g of a mixture comprising 2% FC-1, 3% acetic acid, 10% water and 85% ethanol. In example 5, 100 g dry quartz was treated with 3 g FC-3, dissolved in 20 g ethylacetate. The mixtures were mixed with a spatula during 5 min and dried at 120°C during 15 minutes. 60 g of the treated quartz was mixed with 40 g Portland cement. 20-30 g water were added and the compounds were mixed with a spatula to obtain a homogeneous composition. The grout was applied between pre-glued tiles and dried according to the general procedure. The dried grout was evaluated for oil and water repellency, before and after abrasion. The results of the contact angles are given in table 2.

Table 2 :

Contact angles of grout obtained from grout powder, comprising quartz treated with a fluoro chemical compound					
Ex	Fluorochemical compound	Contact angles (°)			
		Initial Water	Initial hexadecane	Abrasion water	Abrasion hexadecane
4	FC-1	96	65	70	52
5	FC-3	80	55	65	45

[0048] The results in table 2 show that grout powder, made from quartz, treated with fluorochemical compound, and untreated Portland cement, provided a grout composition that had high oil- and water repellency, not only initially, but also after abrasion. High durable oil- and water repellent compositions were made.

Example 6

[0049] In example 6, 100 g Portland cement was mixed with 100 g of a composition comprising 2% FC-1, 3% acetic acid, 10% water and 85% ethanol. After mixing for 5 min, the cement was dried at 120°C during 15 minutes. 40 g of the treated cement was mixed with 60 g untreated quartz. 20-30 g water were added and the compounds were mixed with a spatula to obtain a homogeneous composition. The grout was applied between pre-glued tiles and dried according to the general procedure. The dried grout was evaluated for oil and water repellency, before and after abrasion. The results of the contact angles are given in table 3.

Table 3 :

Contact angles of grout obtained from grout powder comprising Portland cement treated with a fluorochemical compound					
Ex	Fluorochemical compound	Contact angles (°)			
		Initial Water	Initial hexadecane	Abrasion water	Abrasion hexadecane
6	FC-1	85	60	70	50

[0050] The results indicate that grout, made from grout powder, comprising Portland cement, treated with a fluorochemical treating agent, had high oil and water repellency, not only initially, but also after abrasion.

Examples 7 and 8

[0051] In example 7, 10 g glassbubbles were mixed with 100 g of a solution comprising 2% FC-1, 3% acetic acid, 10% water and 85% ethanol. In example 8, FC-4 was dried to 100% solids ; 3 g solids were redissolved in 20 g HFE 7100. This solution was mixed with 10 g glassbubbles. After mixing for 5 min, the glassbubbles were dried at 120°C during 15 minutes. 5 g of the treated glassbubbles were mixed with 100 g grout powder, comprising 40% Portland cement and 60% quartz. After the addition of water and mixing to obtain a homogeneous composition, the grout was applied according to the general procedure.

[0052] Dried grout was tested for oil and water repellency. The contact angles, measured before and after abrasion are recorded in table 4.

Table 4 :

Contact angles of grout obtained from grout powder comprising glassbubbles treated with fluorochemical compound					
Ex	Fluorochemical compound	Contact angles (°)			
		Initial Water	Initial hexadecane	Abrasion water	Abrasion hexadecane
7	FC-1	95	60	80	50
8	FC-4	98	63	80	54

[0053] The results indicate that grout having high oil- and water repellency, both initially and also after abrasion, could be made when the grout powder was mixed with glassbubbles, that had been treated with fluorochemical compound.

5 Examples 9 and 10

[0054] In example 9, 100 g dry grout powder, comprising 40% Portland cement and 60% quartz, was mixed with 1 g FC-5, dissolved in 100 g HFE. After mixing with a spatula for 5 min, the treated grout powder was dried at 120°C during 15 min. In example 10, 100 g dry quartz was mixed with 1 g FC-5, dissolved in 100 g HFE. After mixing for 5 min, the treated quartz was dried at 120°C during 5 min. 60 g of the treated quartz was mixed with 40 g Portland cement to produce grout powder. Water was added to the grout powders of examples 9 and 10 and the compositions were mixed to form homogeneous grout. The grout was applied between pre-glued tiles and dried according to the general procedure. The dried grout was evaluated for oil and water repellency, before and after abrasion. The results of the contact angles are given in table 5.

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Table 5 :

Contact angles of grout obtained from grout powder or quartz treated with fluorochemical compound.					
Ex	Treated compound	Contact angles (°)			
		Initial Water	Initial hexadecane	Abrasion water	Abrasion hexadecane
9	Grout powder	92	44	90	30
10	Quartz	90	57	78	35

25 [0055] As can be seen from the results, grout with good oil and water repellency could be made.

Claims

- 30 1. Grout powder for admixture with water to produce grout, said grout powder comprising cement powder, characterized in that said grout powder has been mixed with a fluorochemical compound.
2. Grout powder according to claim 1 wherein at least one of the components of the grout powder has been treated on its surface with said fluorochemical compound.
- 35 3. Grout powder according to claim 2, wherein said cement powder is surface treated with said fluorochemical compound.
4. Grout powder according to claim 3, wherein said grout powder further comprises quartz particles that are optionally surface treated with said fluorochemical compound.
- 40 5. Grout powder according to any of the previous claims, further comprising glass bubbles that are optionally surface treated with said fluorochemical compound.
6. Grout powder according to any of the previous claims wherein said grout powder contains said fluorochemical compound in an amount of 0.05% to 5% by weight on the total weight of grout powder.
- 45 7. Grout powder according to any of the previous claims wherein said fluorochemical compound has a functional group capable of reacting with the surface of one or more components of said grout powder.
- 50 8. Grout powder according to claim 7, wherein said functional group is an acid group or a silane group.
9. Grout powder according to claim 8 wherein said fluorochemical compound corresponds to the formula:

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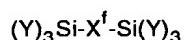
wherein R_f represents a fluorinated organic group, Y represents an alkyl group, an aryl group, or a hydrolysable group, each Y group being the same or different and at least one Y group being a hydrolysable group and n being 1 or 2.

- 5 10. Grout powder according to claim 9, wherein R_f corresponds to the formula:



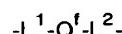
10 wherein X represents an organic linking group or a chemical bond, R_f^a represents a perfluorinated aliphatic group having at least 3 carbon atoms, a perfluorinated or partially fluorinated polyether or a fluorinated oligomer of the formula M^f_sM^h_t wherein M^f represents units derived from a fluorinated monomer, M^h represents units derived from non-fluorinated monomers, s represents a value of 1 to 40, t represents a value of 0 to 40 and the sum of s and t is at least 2.

- 15 11. A grout powder according to claim 8 wherein said fluorochemical compound corresponds to the formula:



20 wherein Y represents an alkyl group, or a hydrolysable group, each Y group being the same or different and at least one Y group being a hydrolysable group and X^f representing a fluorinated or perfluorinated organic divalent group.

- 25 12. A grout powder according to claim 11 wherein X^f represents a divalent fluorinated or perfluorinated polyether containing organic group or wherein X^f corresponds to the formula:



30 wherein L¹ and L² each independently represents an organic divalent linking group or a chemical bond and Q^f represents a perfluorinated aliphatic group of at least 3 carbon atoms.

- 35 13. Method of preparing grout powder for admixture with water to produce grout, comprising mixing grout powder comprising cement powder with a fluorochemical compound.

- 40 14. Method of preparing grout powder for admixture with water to produce grout, said grout powder comprising cement powder, said method comprising the step of treating at least one of the components of said grout powder with a fluorochemical compound.

- 45 15. Grout comprising a mixture of grout powder and water characterized in further comprising a fluorochemical compound.

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EUROPEAN SEARCH REPORT

Application Number
EP 01 20 2026

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